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Theoretical Studies of Atmospheric Molecules: SCF and Correlated Energy Levels for the NO_2, NO_2^+ and NO_2^- Systems*

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SCF and MC-SCF/CI calculations were carried out on the low-lying electronic states of NO_2, NO_2^+ and NO_2^-, using a double-zeta quality basis set of contracted Gaussian functions. The calculations were performed primarily at the equilibrium geometry ($R_{NO}=2.25\ a_0$, $\theta_{ONO}=134°$) of the X^2A_1 state of NO_2. SCF calculations on NO_2^+ in a linear conformation were also performed. Results are presented and compared with experiment and other calculations.

Key words: NO_2, NO_2^+, and NO_2^-, SCF and MC-SCF/CI calculations of ~

1. Introduction

The aeronomical significance of NO_2 and NO_2^+ has been known for some time [1–3]. For this reason, among others, a large number of experimental and theoretical studies, especially on the NO_2 system, have been carried out. The NO_2^+ system has not been studied so prolifically, and proportionately less is known about it. In fact, the dominant amount of information on this ion has resulted from ionization potential studies on NO_2. Most of these studies have been experimental, including electron impact, photoionization, and photoelectron spectroscopy [4]. The paucity of computational results has made the assignment of the NO_2^+ spectrum difficult. In fact, most spectral assignments have been based on the semi-empirical calculations of McEwen [5] and Burnelle *et al.* [6], the SCF calculations of Brundle *et al.* [7], as well as that information which can be inferred

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from knowledge of the energy spectrum of CO_2 (with which NO_2^+ is isoelectronic). The work of Brundle *et al.* was primarily an experimental study, but included SCF calculations on the X^2A_1 state of NO_2 and the X^1A_1 ($^1\Sigma_g^+$) state of NO_2^+ as an integral part. The excitation energies for NO_2^+ were then estimated from the orbital energies obtained in the calculation on the X^1A_1 state. Pfeiffer and Allen also carried out SCF calculations on the ground state of NO_2^+, including angle variations and analysis of the resulting Walsh diagrams [8]. In none of these calculations, however, was the electronic spectrum constructed from individual calculations on the various excited states of NO_2^+.

As part of a systematic study of the atmospheric molecules H_2O, NO_2, CO_2, O_3, and N_2O and their singly charged ions, we have carried out SCF and MC-SCF/CI calculations [9] on the low-lying electronic states of NO_2, NO_2^+, and NO_2^-, at the experimental equilibrium geometry of NO_2 ($R_{NO}=2.25\ a_0$, $\theta_{ONO}=134°$) [10], using Dunning's [4s, 3p] basis set of contracted Gaussian type functions [11]. We have also included SCF calculations at this same bond length and $\theta_{ONO}=180°$ for NO_2^+. The results of these calculations represent heretofore unavailable data for the electronic spectra of these systems. Comparison of our results with experiment and other calculations, such as they exist, is made.

A review of the current state of knowledge on the species of interest in this paper, as well as the additional triatomics mentioned above can be found in Ref. [12].

2. Calculations

The computation of the energy of each electronic state considered proceeded as follows: using the [4s, 3p] basis set, an SCF calculation was performed. Following this, an initial MC-SCF calculation was carried out in which the configuration list consisted of the SCF configuration plus a number of double excitations which were thought to be important based on previous calculations, and which were sufficient to occupy the 15 valence orbitals. The MC-SCF approximations to the valence orbitals which resulted were then used in a CI calculation which included all single and double excitations from the SCF configuration into the valence space, with no excitations allowed from the five lowest-lying orbitals. From the resulting wavefunction, all those configurations with coefficients whose magnitudes exceeded 0.035 were used in an additional MC-SCF calculation. After this second MC-SCF, a final valence space CI was done in which the configuration list consisted of all singles and doubles from the SCF configuration, plus singles and doubles from those configurations which had coefficient magnitudes in the MC-SCF wavefunction exceeding 0.1. Thus, these calculations included the effects of selected triples and quadruples from the SCF configuration. As noted above, the $1a_1$, $2a_1$, $3a_1$, $1b_2$ and $2b_2$ orbitals were frozen in constructing the configuration lists. These correspond to the 1s orbitals on each atom, and the 2s orbitals on the oxygens. The validity of freezing the oxygen 2s orbitals was assessed by allowing excitations from them in the CI calculations for a few of the states. For the states tested, the excitation energies changed by about 0.1 eV. This was felt to be less than the error introduced in other parts of the calculation, and since freezing these orbitals resulted in smaller configuration lists, this effect was ignored. In addition to these restrictions, the programs used did not permit inclusion of configurations with six or more open shells in the MC-SCF calculations. This restriction will be removed in subsequent work.

3. Results and Discussion

Since, as noted above, there are a relatively large number of computations currently available on the NO_2 molecule, our calculations on this molecule serve as a reference with respect to which we can calibrate our basis set and computational method. The pertinent information is summarized in Table 1. Included in this table are excitation energies obtained in the MC-SCF/CI calculations of Gillispie *et al.* [13] and the traditional CI calculations of Hay [14]. The former calculation represents the more accurate of the two, and is therefore of particular interest to us. In their work, Gillispie *et al.* used a [4s, 3p, 1d] Dunning basis set and did not include effects of triple and quadruple excitations from the SCF determinant. Their geometries, harmonic frequencies, and one electron properties compare very well with experiment, and the vibrationally corrected excitation energies are in good agreement with electron impact data. Thus, to the extent that NO_2 is representative of the NO_2^+, NO_2, NO_2^- sequence, the results of Ref. [13] should provide an adequate reference by which the quality of the present results can be assessed.

As can be seen from Table 1, the results of our calculations are in quite good agreement with those of other calculations whose accuracy is established.

It might seem at first sight that the agreement between the results of Ref. [13] and our own work implies that the effects of triple and quadruple excitations can be ignored. This is not necessarily true, however, since the basis sets in the two calculations are not the same. We include the effects of these higher excitations here because their importance will be explicitly assessed in further phases of our program.

In addition to the work in Refs. [13] and [14], a number of other NO_2 calculations of lesser accuracy have been reported, including the recent work of Jackels and

Table 1. NO_2 energy spectrum, [4s, 3p] basis set, $R_{NO} = 2.25\ a_0$, $\theta_{ONO} = 134°$

State	SCF[a]	T_e^{calc} (SCF)[b]	MC-SCF/CI[a]	T_e^{calc} (MC-SCF/CI)[b]	T_e^{calc} (Ref. [14])	T_e^{calc} (Ref. [13])
X^2A_1	−203.95599	0.00	−204.15027	0.00	0.00	0.00
1^2B_1	−203.86422	2.50	−204.05748	2.52	2.45	2.80
1^2B_2	−203.81487	3.84	−204.02800	3.33	3.03	3.40
1^2A_2	−203.85209	2.83	−204.02103	3.52	3.09	3.40
1^4A_2	−203.87780	2.13	−203.98811	4.41	3.81	4.70
1^4B_2	−203.87733	2.14	−203.98567	4.48	3.80	4.60

[a] Units are hartrees. [b] Units are electron volts.

Davidson [21]. In this last work, a double zeta basis set of Gaussian lobe functions was used in CI calculations on the potential surfaces of 16 states. Vertical excitation energies were calculated at the computed ground state equilibrium geometry ($R_{NO}=2.35\ a_0$, and $\theta_{NO}=132.99°$). The numbers obtained differ significantly from the present ones (computed at the experimental equilibrium geometry) as well as those of Refs. [13] and [14]. However, the potential surface results, including determination of potential surface interactions, of Ref. [21] represent the most extensive set to date.

The main system of interest in this work is the NO_2^+ system. The pertinent results obtained in our calculations are presented in Table 2. The first thing to be noted in this table is that, like the 1^2B_2 and 1^4A_2 states of NO_2, the relative position of the X^1A_1 state of NO_2^+ is incorrectly predicted by the SCF calculations. Since NO_2^+ is isoelectronic with CO_2 and linear by all of the Mulliken-Walsh rules, it might be expected that this reordering is due to the fact that we are far from the equilibrium geometry of the ground state and have encompassed a $X^1A_1 - 1^3B_2$ level crossing. That this is not the case in the real ion is seen from the correlated results, in which as expected the lowest $^1A_1$ state is seen to correspond to the ground state. This illustrates the often-observed fact that in the SCF approximation, electronic states can appear inverted.

In Table 3, the SCF results for linear NO_2^+ are presented. Here, we see that the SCF ground state now corresponds correctly to the $X^1\Sigma_g^+$ (X^1A_1) state.

Table 2. NO_2^+ energy spectrum, [4s, 3p] basis set, $R_{NO}=2.25\ a_0$, $\theta_{ONO}=134°$

State	SCF[a]	T_e^{calc} (SCF)[b]	MC-SCF/CI[a]	T_e^{calc} (MC-SCF/CI)[b]	T_e^{expt} [c]
X^1A_1	−203.50085	0.90	−203.79836	0.0	0.0
1^3B_2	−203.53422	0.00	−203.70433	2.56	1.78
1^3A_2	−203.48503	1.34	−203.70079	2.65	2.37
1^1A_2	−203.46880	1.78	−203.66766	3.55	2.83
1^1B_2	−203.38226	4.13	−203.65717	3.84	3.28
1^3A_1	−203.26660	7.28	−203.54723	6.83	6.22
1^3B_1	−203.23035	8.27	−203.51535	7.70	6.41
1^1B_1	−203.19303	9.28	−203.47550	8.78	—

[a] Units are hartrees.
[b] Units are electron volts.
[c] Ref. [7].

Table 3. NO_2^+ SCF energy spectrum, [4s, 3p] basis set, $R_{NO}=2.25\ a_0$, $\theta_{ONO}=180°$

State	SCF Energy[a]	T_e^{calc} (SCF)[b]
$X^1\Sigma_g^+$	−203.54765	0.0
$^3\Sigma_u^+$	−203.45745	2.45
$^3\Delta_u$	−203.43211	3.14
$^1\Sigma_u^-$	−203.40746[c]	3.81
$^3\Sigma_u^-$	−203.40746[c]	3.81
$^1\Sigma_u^+$	−203.39159	4.25
$^1\Delta_u$	−203.39090	4.27

[a] Units are hartrees.
[b] Units are electron volts.
[c] The SCF energies for the $^1\Sigma_u^-$ and $^3\Sigma_u^-$ states must be the same, as they are defined by the same Fock equations.

It is apparent that, while the ordering of the states given in Table 2 agrees with that of Brundle *et al.*, the actual excitation energies differ significantly. Certainly, the use of a limited basis set coupled with residual correlation errors account for some of the discrepancies. Based on the NO_2 results, however, these do not account for the sizes of the observed differences. In Ref. [13], agreement with excitations taken from electron impact experiments required computation of vibrational effects. This is probably the main source of difference between the computed and experimental numbers in the present calculations. At the outset we can expect a significant difference between T_e^{calc} and T_e^{expt} due to vibrational effects, since the equilibrium geometry of the neutral ground state (bent) and that of the ion (linear) are significantly different. Thus the largest Franck-Condon factor will probably correspond to a transition to an excited vibrational state in the ion ground state. This effect is, of course, not present in the numbers in Table 2.

A similar situation occurs and has been analyzed in the case of the photoelectron spectrum of H_2O [15]. In the case of H_2O, however, the neutral and ion ground states have similar geometries while the excited state ion geometries differ significantly from either. The vibrational effect is observed to give rise to discrepancies which are greater than 1 eV between the energy differences of computed electronic states of the ion and the differences between PES peaks [15].

A second point relating to the peak assignments in Ref. [7], involves the use of SCF calculations. Aside from the well-known errors associated with SCF calculations, one is generally unable, using the usual form of the SCF procedure, to obtain reliable estimates for excited states which lie above other states having the same overall symmetry. This is due to variational collapse into the lower state. The use of upper roots of multiconfiguration approaches overcomes this limitation and provides rigorous upper bounds for each electronic energy level.

In the present work, estimates of the lowest lying of these states were obtained by taking the second root of the secular determinant constructed from the orbitals and configuration lists which are appropriate for the lowest state of each symmetry. As such, the results obtained represent rigorous upper bounds to the corresponding excited states. However, since the orbitals and CI lists were not chosen from explicit consideration of the states of interest, the values for T_e^{calc} are undoubtedly high. Nonetheless, it is of interest to note that *all* of the second roots for the NO_2^+ states listed in Table 2 lie within 15 eV of the computed energy of the X^1A_1 state. This is significant because in the PES experiments of Ref. [7], the ionization potentials of NO_2 up to 28 eV were measured. This encompasses states up to about 17 eV above the X^1A_1 appearance potential. In that work, the 2^3B_2, 2^1B_1, and 2^3A_1 states were assigned to peaks corresponding to T_e^{expt} values of 7.63 eV, 9.77 eV, and 10.03 eV, respectively. The T_e^{calc} values for these states are 7.18 eV, 10.38 eV, and 8.61 eV, respectively. Two additional low-lying states, not assigned in Ref. [7], the 1^1B_1 ($T_e^{\text{calc}} = 8.78$ eV) and the 2^3A_2 ($T_e^{\text{calc}} = 8.04$ eV), should also be noted.

As indicated above, the T_e^{calc} values for these states (except for the 1^1B_1) are necessarily high, and not of the same accuracy as the corresponding values for the lowest state of each symmetry. Nonetheless, the existence of these states within 8–10 eV of the ground state should be kept in mind when considering the PES measurements. It is true, however, that the Franck-Condon factors for these states may be sufficiently small so that the intensities are weak, and not detectable in a PES experiment.

To date, calculations on the various electronic states of the NO_2^- ion have been carried out via semi-empirical techniques [16, 17]. The SCF results obtained in the present calculations are presented in Table 4. Values for the electron affinity of NO_2 vary from about 2.28 eV to about 2.36 eV [18–20]. For comparison, the computed SCF vertical electron affinity is 0.93 eV. The disagreement between this number and the measured values is due in part to the inadequacy of the SCF model, and in part to the lack of diffuse functions in the basis set. The experimental θ_{ONO} for NO_2^- is ~20° smaller than θ_{ONO} of neutral NO_2 [12], and for this reason also the computed vertical electron affinity is expected to be smaller than the observed electron affinity. The inadequacy of the SCF model is expected to be particularly serious for a molecule like NO_2, as the "extra" electron completes a shell (the $6a_1$), so that the correlation energy in the NO_2 molecule would not be expected to be the same as that in the NO_2^- ion. This means that the SCF approximation is not as good as it might be when an electron is added outside of a closed shell. This latter situation is the case, for example, in N_2O where the SCF electron affinity is quite good. An alternate method of computing the vertical electron affinity amounts to applying Koopmans' theorem to the negative ion and taking the electron affinity to be equal to $-E_{6a_1}(NO_2^-)$. This results in a value of 2.16 eV for the electron affinity of NO_2. This is quite close to the experimental value, and may reflect the mutual cancellation of charge reorganization effects and electron correlation effects. However, this agreement is somewhat fortuitous due to lack of diffuse functions in the basis set. In any case, the SCF excitation energies can be very useful in terms of a qualitative description. This is particularly so since little is known about the electronic states of this ion at the present time.

Table 4. NO_2^- SCF energy spectrum, [4s, 3p] basis set, $R_{NO} = 2.25\ a_0$, $\theta_{ONO} = 134°$

State	SCF Energy[a]	T_e^{calc} (SCF)[b]
X^1A_1	−203.99028	0.00
1^3B_1	−203.95430	0.98
1^1B_1	−203.89964	2.47
1^3B_2	−203.83892	4.12
1^3A_2	−203.78432	5.60
1^1A_2	−203.77247	5.92
1^1B_2	−203.68674	8.26
1^3A_1	−203.63651	9.62

[a] Units are hartrees.
[b] Units are electron volts.

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